(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
4 July 2002 (04.07.2002)

PCT

(10) International Publication Number
WO 02/051616 A2

(51) International Patent Classification[7]: B29C 47/00

(21) International Application Number: PCT/US01/48440

(22) International Filing Date: 14 December 2001 (14.12.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

09/738,619	15 December 2000 (15.12.2000)	US
09/932,150	17 August 2001 (17.08.2001)	US
10/017,400	14 December 2001 (14.12.2001)	US

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier applications:

US	10/017,400 (CON)
Filed on	14 December 2001 (14.12.2001)
US	09/932,150 (CIP)
Filed on	17 August 2001 (17.08.2001)
US	09/738,619 (CIP)
Filed on	15 December 2000 (15.12.2000)

(71) Applicant (for all designated States except US): WELLMAN, INC. [US/US]; 1040 Broad Street, 302, Shrewsbury, NJ 07702-4318 (US).

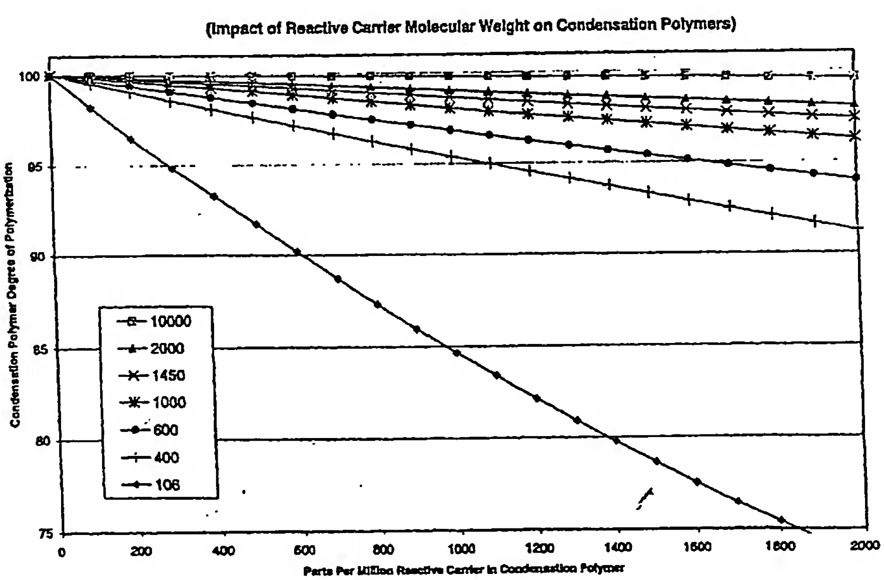
(72) Inventors; and
(75) Inventors/Applicants (for US only): NICHOLS, Carl, Steven [US/US]; 10410 New Town Road, Waxhaw, NC 28173 (US). MOORE, Tony, Clifford [US/US]; 5210 Carmel Park Drive, Charlotte, NC 28226 (US). SCHIAVONE, Robert, Joseph [US/US]; 221 Sardis Point Road, Matthews, NC 28105 (US). EDWARDS, Walter, Lee [US/US]; 7739 Fruitwood Court, Harrisburg, NC 28075 (US).

(74) Agents: ADDITON, Richard, L. et al.; Summa & Allan, P.A., 11610 N. Community House Road, Suite 200, Ballantyne Corporate Park, Charlotte, NC 28277 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO,

[Continued on next page]

(54) Title: METHODS OF POST-POLYMERISATION EXTRUDER INJECTION IN CONDENSATION POLYMER PRODUCTION



(57) Abstract: The invention is a novel method for the late introduction of additives into condensation polymers. The method employs a reactive carrier that functions as a delivery vehicle for one or more additives. The reactive carrier reacts with the condensation polymers, thereby binding the reactive carrier in the polymer resin and preventing the emergence of the reactive carrier from the polymer resin during subsequent thermal processing.

WO 02/051616 A2

NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) **Designated States** *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report*

METHODS OF POST-POLYMERIZATION EXTRUDER INJECTION IN CONDENSATION POLYMER PRODUCTION

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation-in-part of U.S. application Ser. No. 09/932,150, for *Methods of Post-Polymerization Extruder Injection In Polyethylene Terephthalate Production*, filed August 17, 2001, which itself is a continuation-in-part of copending and commonly-assigned U.S. application Ser. No. 09/738,150, for *Methods of Post-Polymerization Injection in Continuous Polyethylene Terephthalate Production*, filed December 15, 2000. This application is also related to concurrently-filed application Ser. No. ________ for *Methods of Post-Polymerization Injection in Condensation Polymer Production.* Each of these pending applications is commonly assigned with this application and is hereby incorporated entirely herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to the processing of condensation polymers. More particularly, the present invention relates to the late introduction of additives into condensation polymers via reactive carriers.

BACKGROUND OF THE INVENTION

[0003] Because of their strength, heat resistance, and chemical resistance, polyester fibers and films are an integral component in numerous consumer products manufactured worldwide. Most commercial polyester used for polyester fibers and films is polyethylene

terephthalate (PET) polyester. Because polyethylene terephthalate forms a lightweight and shatterproof product, another popular use for polyethylene terephthalate is as a resin for containers, especially beverage bottles.

[0004] Before 1965, the only feasible method of producing polyethylene terephthalate polyester was to use dimethyl terephthalate (DMT). In this technique, dimethyl terephthalate and ethylene glycol are reacted in a catalyzed ester interchange reaction to form bis(2-hydroxyethyl) terephthalate monomers and oligomers, as well as a methanol byproduct that is continuously removed. These bis(2-hydroxyethyl)terephthalate monomers and oligomers are then polymerized via polycondensation to produce polyethylene terephthalate polymers.

[0005] Purer forms of terephthalic acid (TA) are now increasingly available. Consequently, terephthalic acid has become an acceptable, if not preferred, alternative to dimethyl terephthalate as a starting material for the production of polyethylene terephthalate. In this alternative technique, terephthalic acid and ethylene glycol react in a generally uncatalyzed esterification reaction to yield low molecular weight monomers and oligomers, as well as a water byproduct that is continuously removed. As with the dimethyl terephthalate technique, the monomers and oligomers are subsequently polymerized by polycondensation to form polyethylene terephthalate polyester. The resulting polyethylene terephthalate polymer is substantially identical to the polyethylene terephthalate polymer resulting from

dimethyl terephthalate, albeit with some end group differences.

[0006] Polyethylene terephthalate polyester may be produced in a batch process, where the product of the ester interchange or esterification reaction is formed in one vessel and then transferred to a second vessel for polymerization. Generally, the second vessel is agitated and the polymerization reaction is continued until the power used by the agitator reaches a level indicating that the polyester melt has achieved the desired intrinsic viscosity and, thus, the desired molecular weight. More commercially practicable, however, is to carry out the esterification or ester interchange reactions, and then the polymerization reaction as a continuous process. The continuous production of polyethylene terephthalate results in greater throughput, and so is more typical in large-scale manufacturing facilities.

[0007] When the polymerization process is complete, the resulting polymer melt is typically extruded and pelletized for convenient storage and transportation before being transformed into specific polyester articles (e.g., filament, films, or bottles). The latter kinds of steps are herein referred to as "polyester processing."

[0008] In both batch and continuous processes, a high activity catalyst is often employed to increase the rate of polymerization, thereby increasing the throughput of the resulting polyethylene terephthalate polyester. The high activity catalysts that are used in the polymerization of polyethylene terephthalate polyester

can be basic, acidic, or neutral, and are often metal catalysts.

[0009] Primarily, the traditional polymerization catalysts used in the formation of polyethylene terephthalate from both terephthalic acid and dimethyl terephthalate contain antimony, most commonly antimony trioxide (Sb_2O_3). Although increasing production rates, polymerization catalysts like antimony trioxide will eventually begin to catalyze or encourage the degradation of the polyethylene terephthalate polymer. Such polymer degradation results in the formation of acetaldehyde, the discoloration (e.g., yellowing) of the polyethylene terephthalate polyester, and reduction of polymer molecular weight.

[0010] Furthermore, the recent availability of "hotter" catalysts that can significantly increase throughput has generated a corresponding need for better stabilization of the resulting polyester. U.S. Patent No. 5,008,230 for a *Catalyst for Preparing High Clarity, Colorless Polyethylene Terephthalate* is exemplary of such an improved catalyst. To reduce the degradation and discoloration of polyethylene terephthalate polyester, stabilizing compounds are used to sequester ("cool") the catalyst, thereby reducing its effectiveness. The most commonly used stabilizers contain phosphorous, typically in the form of phosphates and phosphites. The phosphorous-containing stabilizers were first employed in batch processes to prevent degradation and discoloration of the polyethylene terephthalate polyester.

[0011] Although adding a stabilizer to the polymer melt in a batch reactor is a relatively simple process, numerous problems arise if the stabilizers are added in the continuous production of polyethylene terephthalate. For example, while early addition of the stabilizer prevents discoloration and degradation of the polyester, it also causes reduced production throughput (*i.e.*, decreases polycondensation reaction rates). Moreover, such stabilizer is typically dissolved in ethylene glycol, the addition of which further slows the polymerization process. Consequently, early addition of the stabilizer in the polymerization process requires an undesirable choice between production throughput and thermal stability of the polymer. As used herein, "thermal stability" refers to a low rate of acetaldehyde generation, low discoloration, and retention of molecular weight following subsequent heat treatment or other processing.

[0012] Late addition of the stabilizer (e.g., after the polymerization process during polymer processing) may provide insufficient opportunity for the stabilizer to fully blend with the polymer. Consequently, the stabilizer may not prevent degradation and discoloration of the polyester. In addition, adding stabilizer during polymer processing is inconvenient and does not provide economies of scale.

[0013] U.S. Patent No. 5,376,702 for a *Process and Apparatus for the Direct and Continuous Modification of Polymer Melts* discloses dividing a polymer melt stream into an unmodified stream and a branch stream that receives additives. In particular, a side stream takes a

portion of the branch stream to an extruder, where additives are introduced. Such techniques, however, are not only complicated, but also costly, requiring a screw extruder and melt piping to process additives. Consequently, such arrangements are inconvenient and even impractical where total additive concentrations are low (e.g., less than one weight percent).

[0014] Certain problems associated with late addition of stabilizer are addressed in U.S. Patent No. 5,898,058 for a *Method of Post-Polymerization Stabilization of High Activity Catalysts in Continuous Polyethylene Terephthalate Production*, which discloses a method of stabilizing high activity polymerization catalysts in continuous polyethylene terephthalate production. This patent, which is commonly assigned with this application, is hereby incorporated entirely herein by reference.

[0015] In particular, U.S. Patent No. 5,898,058 discloses adding a stabilizer, which preferably contains phosphorous, at or after the end of the polymerization reaction and before polymer processing. This deactivates the polymerization catalyst and increases the throughput of the polyester without adversely affecting the thermal stability of the polyethylene terephthalate polyester. While a noteworthy improvement over conventional techniques, U.S. Patent No. 5,898,058 teaches adding the stabilizer without a carrier. Consequently, the addition of solids into the polymer necessitates the costly use of an extruder.

[0016] U.S. parent application Ser. No. 09/738,150 for *Methods of Post-Polymerization Injection in Continuous*

Polyethylene Terephthalate Production, discloses a process for the production of high quality polyethylene terephthalate polyester that improves upon the stabilizer-addition techniques disclosed by commonly-assigned U.S. Patent No. 5,898,058.

[0017] More specifically, U.S. application Ser. No. 09/738,150 discloses a method for the late introduction of additives into a process for making polyethylene terephthalate. The additives are introduced during, and preferably after, the polycondensation of polyethylene terephthalate polymers. In particular, the method employs a reactive carrier that not only functions as a delivery vehicle for one or more additives, but also reacts with the polyethylene terephthalate, thereby binding the carrier in the polyethylene terephthalate resin. Moreover, U.S. application Ser. No. 09/738,150 discloses that this may be achieved using a simplified additive delivery system that does not require the use of an extruder.

[0018] The technology of U.S. application Ser. No. 09/738,150 is effectively employed in co-pending and commonly-assigned application U.S. Ser. No. 09/738,619 for *Polyester Bottle Resins Having Reduced Frictional Properties and Methods for Making the Same*, which was also filed December 15, 2000, and which is herein incorporated by reference in its entirety. U.S. application Ser. No. 09/738,619, in certain preferred embodiments, likewise employs a simplified additive delivery system that does not require the use of an extruder.

[0019] Despite the preference to exclude an extruder from additive delivery systems, there are circumstances where using an extruder is advantageous. For example, introducing additives at an extruder facilitates quick formulation changes. Moreover, while introducing additives at an extruder may hinder productivity at larger-scale operations, it may be appropriate for smaller-scale operations.

[0020] Accordingly, U.S. application Ser. No. 09/932,150, for *Methods of Post-Polymerization Extruder Injection in Polyethylene Terephthalate Production*, which is a continuation-in-part of U.S. parent application Ser. No. 09/738,150, discloses a method for late additive introduction at an extruder during a process for making polyethylene terephthalate. In particular, the method employs a reactive carrier that not only functions as a delivery vehicle for one or more additives, but also reacts with the polyethylene terephthalate to bind the carrier in the polyethylene terephthalate resin. This not only prevents the emergence of the carrier from the polyethylene terephthalate during subsequent processing (*e.g.*, solid state polymerization, drying operations, and injection molding operations), but also improves dispersion of the additive in the polymer and reduces the tendency of the additive to emerge and deposit in polymer processing equipment during solid state polymerization.

[0021] The method of U.S. application Ser. No. 09/932,150 has application to the production of condensation polymers generally. There is, in fact, a need for a post-polymerization injection technique that ensures that the late addition of additives during

polymer processes will yield condensation polymers whose additives and carriers are integral parts of the condensation polymer resin, while retaining the conveniences associated with extruder addition.

SUMMARY OF THE INVENTION

[0022] Accordingly, it is an object of the present invention to provide a method of adding additives to condensation polymers at an extruder via a reactive carrier.

[0023] It is a further object of the present invention to provide a method of adding additives to condensation polymers via a reactive carrier in a way that permits quick formulation changes.

[0024] It is a further object of the present invention to provide a method of adding additives to condensation polymers via a reactive carrier in order to reduce polymer transition times and eliminate process upsets resulting from changing polymer formulations.

[0025] It is a further object of the present invention to provide a method of introducing additives into condensation polymers in a way that reduces the degradation or volatilization of such additives.

[0026] The foregoing, as well as other objectives and advantages of the invention and the manner in which the same are accomplished, is further specified within the following detailed description and its accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS:

[0027] Figure 1 illustrates the theoretical loss of molecular weight (as measured by number-average degree of polymerization) for condensation polymers having an initial degree of polymerization of about 100 as a function of the concentration of the reactive carrier at various molecular weights.

[0028] Figure 2 illustrates the theoretical loss of molecular weight (as measured by number-average degree of polymerization) for condensation polymers having an initial degree of polymerization of about 70 as a function of the concentration of the reactive carrier at various molecular weights.

[0029] Figure 3 illustrates the theoretical loss of intrinsic viscosity of polyethylene terephthalate having an intrinsic viscosity of 0.63 dl/g as a function of the concentration of the reactive carrier at various molecular weights.

[0030] Figure 4 illustrates the theoretical loss of intrinsic viscosity of polyethylene terephthalate having an intrinsic viscosity of 0.45 dl/g as a function of the concentration of the reactive carrier at various molecular weights.

DETAILED DESCRIPTION

[0031] The invention is a novel method for late additive introduction at an extruder during the processing of condensation polymers (*i.e.*, one or more additives are introduced into the condensation polymers

by way of a reactive carrier). As noted previously, the method employs a reactive carrier that not only functions as a delivery vehicle for one or more additives, but also reacts with the condensation polymers to bind the reactive carrier in the polymer resin. This prevents the emergence of the carrier from the condensation polymers during subsequent processing, such as solid state polymerization, drying operations, spinning operations, film extrusion, and injection molding operations. This also improves dispersion of the additive in the condensation polymers and reduces the tendency of the carrier to deposit in polymer processing equipment during solid state polymerization.

[0032] The present invention includes combining at an extruder condensation polymers having carbonyl functionality and a reactive carrier having a molecular weight of less than about 10,000 g/mol and being the delivery vehicle for one or more additives.

[0033] In a related aspect, the present invention includes first polymerizing oligomeric precursors via melt phase polycondensation to form condensation polymers having carbonyl functionality. Thereafter, one or more additives are introduced into the condensation polymers at an extruder by way of a reactive carrier that has a molecular weight of less than about 10,000 g/mol.

[0034] As used herein, the concept of combining (or introducing, adding, etc.) the condensation polymers and the reactive carrier at an extruder embraces (1) introducing both the condensation polymers and the reactive carrier into the extruder; (2) introducing the

reactive carrier into the condensation polymers before the extruder, and then mixing the condensation polymers and the reactive carrier within the extruder; and (3) introducing the reactive carrier into the condensation polymers after the extruder.

[0035] As used herein, the term "carbonyl functionality" refers to a carbon-oxygen double bond that is an available reaction site. Condensation polymers having carbonyl functionality are typically characterized by the presence of a carbonyl functional group (*i.e.*, C=O) with at least one adjacent hetero atom (*e.g.*, an oxygen atom, a nitrogen atom, or a sulfur atom) functioning as a linkage within the polymer chain. Accordingly, "carbonyl functionality" is meant to embrace various functional groups including, without limitation, esters, amides, imides, carbonates, and urethanes.

[0036] Suitable polycondensation polymers according to the present invention include, without limitation, polyesters, polyurethanes, polycarbonates, polyamides, and polyimides. Polyesters, such as polyethylene terephthalate, polytrimethylene terephthalate, polybutylene terephthalate, are preferred.

[0037] As will be understood by those of ordinary skill in the art, oligomeric precursors to condensation polymers may be formed by reacting a first polyfunctional component and a second polyfunctional component. For example, oligomeric precursors to polycarbonates may be formed by reacting diols and derivatives of carbonic acid, oligomeric precursors to polyurethanes may be formed by reacting diisocyanates and diols, oligomeric

precursors to polyamides may be formed by diacids and diamines and oligomeric precursors to polyimides may be formed by reacting dianhydrides and diamines. *See, e.g.*, Odian, Principles of Polymerization, (Second Edition 1981). These kinds of reactions are well understood by those of ordinary skill in the polymer arts and will not be further discussed herein.

[0038] It will be further understood by those having ordinary skill in the art that certain monomers possessing multi-functionality can self-polymerize to yield condensation polymers. For example, amino acids and nylon salts are each capable of self-polymerizing into polyamides, and hydroxy acids (*e.g.*, lactic acid) can self-polymerize into polyesters (*e.g.*, polylactic acid).

[0039] Polyesters are the preferred polycondensation polymers, and so the present invention is herein described with particular reference to the introduction of additives into a process for making polyethylene terephthalate. In this regard, oligomeric precursors to polyesters may be formed by reacting diacids and diols or by reacting diesters and diols. The diols may be either aliphatic or aromatic.

[0040] It will be apparent to those of ordinary skill in the polymer arts that the description of the present invention is directed not only to the introduction of additives into polyethylene terephthalate, but also to the introduction of additives into any condensation polymer that possesses carbonyl functionality along its polymer chain. It is expected that an exemplary

description of the invention using a preferred condensation polymer (*i.e.*, polyethylene terephthalate) will enable those skilled in the polymer arts to practice, without undue experimentation, the invention for any condensation polymer having carbonyl functionality. In this regard, those having ordinary skill in the polymer arts will recognize that there are numerous kinds of condensation polymers and copolymers that can be synthesized without departing from the scope and spirit of the present invention.

[0041] The invention preferably includes reacting a terephthalate component and a diol component to form polyethylene terephthalate precursors, *e.g.*, bis(2-hydroxyethyl)terephthalate. These oligomeric precursors are then polymerized via melt phase polycondensation to form polymers of polyethylene terephthalate. During polycondensation, which is usually enhanced by catalysts, ethylene glycol is continuously removed to create favorable reaction kinetics. Thereafter, one or more additives are introduced by way of a reactive carrier into the polyethylene terephthalate polymers (*i.e.*, the reactive carrier functions as an additive delivery vehicle).

[0042] In a particular embodiment of the invention, the polyethylene terephthalate polymers may be pelletized, and thereafter the polyethylene terephthalate polymers and the reactive carrier are introduced at—preferably into—an extruder. The reactive carrier, which has a molecular weight of less than about 10,000 g/mol, not only facilitates uniform blending of the additives within the polymer melt, but also reacts with

the polyethylene terephthalate polymers to ensure that the carrier does not emerge during subsequent processes. The reactive carrier, which, as noted, has a molecular weight of less than about 10,000 g/mol, not only facilitates uniform blending of the additives within the polymer melt, but also reacts with the polyethylene terephthalate polymers to ensure that the carrier does not emerge during subsequent processes.

[0043] As used herein, the term "intrinsic viscosity" is the ratio of the specific viscosity of a polymer solution of known concentration to the concentration of solute, extrapolated to zero concentration. Intrinsic viscosity, which is widely recognized as standard measurements of polymer characteristics, is directly proportional to average polymer molecular weight. *See, e.g., Dictionary of Fiber and Textile Technology*, Hoechst Celanese Corporation (1990); Tortora & Merkel, *Fairchild's Dictionary of Textiles* (7^{th} Edition 1996).

[0044] Intrinsic viscosity can be measured and determined without undue experimentation by those of ordinary skill in this art. For the intrinsic viscosity values described herein, the intrinsic viscosity is determined by dissolving the copolyester in orthochlorophenol (OCP), measuring the relative viscosity of the solution using a Schott Autoviscometer (AVS Schott and AVS 500 Viscosystem), and then calculating the intrinsic viscosity based on the relative viscosity. *See, e.g., Dictionary of Fiber and Textile Technology* ("intrinsic viscosity").

[0045] In particular, a 0.6-gram sample (+/- 0.005 g) of dried polymer sample is dissolved in about 50 ml (61.0 - 63.5 grams) of orthochlorophenol at a temperature of about 105°C. Fiber and yarn samples are typically cut into small pieces, whereas chip samples are ground. After cooling to room temperature, the solution is placed in the viscometer at a controlled, constant temperature, (*e.g.*, between about 20°C and 25°C), and the relative viscosity is measured. As noted, intrinsic viscosity is calculated from relative viscosity.

[0046] The term "diol component" herein refers primarily to ethylene glycol, although other diols (*e.g.*, low molecular weight polyethylene glycol) may be used as well. It will be understood by those of ordinary skill in the art that the diol component usually forms the majority of terminal ends of the polymer chains and so is present in the composition in slightly greater fractions. For example, the molar ratio of the terephthalate component and the diol component is typically between about 1.0:1.0 and 1.0:1.6.

[0047] The term "terephthalate component" herein refers to diacids and diesters that can be used to prepare polyethylene terephthalate. In particular, the terephthalate component mostly includes terephthalic acid and dimethyl terephthalate, but can include diacid and diester comonomers as well. In this regard, those having ordinary skill in the art will know that there are two conventional methods for forming polyethylene terephthalate. These methods are well known to those skilled in the art.

[0048] One method employs a direct esterification reaction using terephthalic acid and excess ethylene glycol. In this technique, the aforementioned step of reacting a terephthalate component and a diol component includes reacting terephthalic acid and ethylene glycol in a heated esterification reaction to form monomers and oligomers of terephthalic acid and ethylene glycol, as well as a water byproduct. To enable the esterification reaction to go essentially to completion, the water must be continuously removed as it is formed.

[0049] The other method involves a two-step ester exchange reaction and polymerization using dimethyl terephthalate and excess ethylene glycol. In this technique, the aforementioned step of reacting a terephthalate component and a diol component includes reacting dimethyl terephthalate and ethylene glycol in a heated ester exchange reaction to form monomers and oligomers of terephthalate and ethylene glycol, as well as methanol as a byproduct. To enable the ester exchange reaction to go essentially to completion, the methanol must be continuously removed as it is formed.

[0050] It will be understood by those having ordinary skill in the art that the polyethylene terephthalate herein described may be a modified polyethylene terephthalate to the extent the diol component includes other glycols besides ethylene glycol, such as diethylene glycol, 1,3-propanediol, 1,4-butanediol and 1,4-cyclohexane dimethanol, or the terephthalate component includes modifiers such as isophthalic acid, 2,6-naphthalene dicarboxylic acid, succinic acid, or one or more functional derivatives of terephthalic acid. In

fact, most commercial polyethylene terephthalate polymers are modified polyethylene terephthalate polyesters.

[0051] In the present invention, the direct esterification reaction is preferred over the older, two-step ester exchange reaction. As noted, the direct esterification technique reacts terephthalic acid and ethylene glycol to form low molecular weight monomers, oligomers, and water.

[0052] For example, in a typical process, the continuous feed enters a direct esterification vessel that is operated at a temperature of between about 240°C and 290°C and at a pressure of between about 5 and 85 psia for between about one and five hours. The reaction, which is typically uncatalyzed, forms low molecular weight monomers, oligomers, and water. The water is removed as the esterification reaction proceeds and excess ethylene glycol is removed to provide favorable reaction kinetics.

[0053] Thereafter, the low molecular weight monomers and oligomers are polymerized via polycondensation to form polyethylene terephthalate polyester. This polycondensation stage generally employs a series of two or more vessels and is operated at a temperature of between about 250°C and 305°C for between about one and four hours. The polycondensation reaction usually begins in a first vessel called the low polymerizer. The low polymerizer is operated at a pressure range of between about 0 and 70 torr. The monomers and oligomers polycondense to form polyethylene terephthalate and ethylene glycol.

[0054] As noted previously, the ethylene glycol is removed from the polymer melt using an applied vacuum to drive the reaction to completion. In this regard, the polymer melt is typically agitated to promote the escape of the ethylene glycol from the polymer melt and to assist the highly viscous polymer melt in moving through the polymerization vessel.

[0055] As the polymer melt is fed into successive vessels, the molecular weight and thus the intrinsic viscosity of the polymer melt increases. The temperature of each vessel is generally increased and the pressure decreased to allow greater polymerization in each successive vessel.

[0056] The final vessel, generally called the "high polymerizer," is operated at a pressure of between about 0 and 40 torr. Like the low polymerizer, each of the polymerization vessels is connected to a flash vessel and each is typically agitated to facilitate the removal of ethylene glycol. The residence time in the polymerization vessels and the feed rate of the ethylene glycol and terephthalic acid into the continuous process is determined in part based on the target molecular weight of the polyethylene terephthalate polyester. Because the molecular weight can be readily determined based on the intrinsic viscosity of the polymer melt, the intrinsic viscosity of the polymer melt is generally used to determine polymerization conditions, such as temperature, pressure, the feed rate of the reactants, and the residence time within the polymerization vessels.

[0057] Note that in addition to the formation of polyethylene terephthalate polymers, side reactions occur that produce undesirable by-products. For example, the esterification of ethylene glycol forms diethylene glycol (DEG), which is incorporated into the polymer chain. As is known to those of skill in the art, diethylene glycol lowers the softening point of the polymer. Moreover, cyclic oligomers (*e.g.*, trimer and tetramers of terephthalic acid and ethylene glycol) may occur in minor amounts. The continued removal of ethylene glycol as it forms in the polycondensation reaction will generally reduce the formation of these by-products.

[0058] Although the foregoing discussion concentrates upon the continuous production of polyester terephthalate polymers, it will be understood that the invention is not so limited. The teachings disclosed herein may be applied to other polycondensation polymers using continuous processes, semi-continuous processes, and even batch processes.

[0059] For instance, the condensation polymers of the present invention are generally filtered and extruded in the melt phase to form polymer sheets, filaments, or pellets. Preferably, the polymer melt is extruded immediately after polycondensation. After extrusion, the polymers are quenched, preferably by spraying with water or immersing in a water trough, to promote solidification. The solidified condensation polymers are cut into chips or pellets for storage and handling purposes. As used herein, the term "pellets" is used generally to refer to chips, pellets, and the like.

[0060] As will be known to those of ordinary skill in the art, the pellets formed from the condensation polymers, in some circumstances, may be subjected to crystallization followed by solid state polymerization (SSP) to increase the molecular weight of the polymer resin. Solid state polymerization can be initiated either before or after introducing the reactive carrier. It should be noted that the inclusion of the reactive carrier does not adversely affect the SSP rate and often will even increase the SSP rate. Thereafter, polymer chips are then re-melted and re-extruded to form items such as containers (*e.g.*, beverage bottles), filaments, films, or other applications. Those of ordinary skill in the art will recognize that certain condensation polymers, such as amorphous polycarbonate, need not undergo SSP.

[0061] The present invention improves upon the prior art by employing a reactive carrier rather than an inert carrier or no carrier at all. The reactive carrier should be introduced to the condensation polymers in quantities such that bulk polymer properties are not significantly affected. The reactive carrier preferably is capable of combining with the condensation polymers such that it is non-extractable during subsequent processing operations.

[0062] Accordingly, in a preferred embodiment, the invention includes introducing to an extruder condensation polymers having carbonyl functionality and a reactive carrier that is the delivery vehicle for one or more additives. Moreover, the reactive carrier, which has an average molecular weight of less than about 10,000

g/mol, is introduced to the extruder in quantities such that bulk polymer properties of the condensation polymers are not significantly affected.

[0063] As used herein, the concept of introducing to an extruder condensation polymers and a reactive carrier embraces (1) introducing both the condensation polymers and the reactive carrier into the extruder; and (2) introducing the reactive carrier into the condensation polymers before the extruder, and then mixing the condensation polymers and the reactive carrier within the extruder.

[0064] Preferably, the reactive carrier has a melting point that ensures that it is a liquid or slurry at about 100°C, which can be achieved using low-pressure steam. Most preferably, the reactive carrier has a melting point that ensures that it is a liquid or slurry at near ambient temperatures. As used herein, the term "near ambient" includes temperatures between about 20°C and 60°C. Near ambient temperatures simplify the unit operations necessary to introduce additives as complicated heating systems are not needed to introduce the reactive carrier into the condensation polymers.

[0065] Because an extruder is employed in the present invention, the condensation polymers are preferably solid (*i.e.*, polymer chips or pellets) when combined with the reactive carrier at the extruder (*e.g.*, introduced into the extruder).

[0066] Likewise, the reactive carrier can be a solid when combined with the condensation polymers at the extruder. In this regard, a solid reactive carrier is

preferably introduced into the extruder toward the back of the extruder as this promotes melting and mixing (and reacting) of the condensation polymers and the reactive carrier.

[0067] Preferably, however, the reactive carrier is a liquid or slurry when combined with the condensation polymers at the extruder. A liquid or slurried reactive carrier can be introduced into the back or front of the extruder. As noted, most preferably, the reactive carrier is a liquid or slurry at near ambient temperatures.

[0068] As a general matter, the reactive carrier should make up no more than about one weight percent of the polymer resin (*i.e.*, 10,000 ppm). Preferably, the reactive carrier is introduced to the condensation polymers in quantities such that its concentration in the polymer resin is less than about 1000 ppm (*i.e.*, 0.1 weight percent). Reducing the reactive carrier to quantities such that its concentration in the polymer resin is less than 500 ppm (*i.e.*, 0.05 weight percent) will further reduce potential adverse effects to bulk polymer properties.

[0069] Figures 1 and 2 illustrate the theoretical loss of molecular weight (as measured by number-average degree of polymerization) as a function of the concentration of the reactive carrier at various molecular weights. Figure 1 depicts the impact of the reactive carrier upon condensation polymers that have an initial degree of polymerization of about 100. Similarly, Figure 2 depicts the impact of the reactive carrier upon condensation

polymers that have an initial degree of polymerization of about 70. (For polyethylene terephthalate, degree of polymerization of about 100 corresponds to an intrinsic viscosity of about 0.61 dl/g and a degree of polymerization of about 70 corresponds to an intrinsic viscosity of about 0.45 dl/g.) Note that at any concentration in a condensation polymer resin, the reactive carriers having higher molecular weights have less adverse effect upon the polymer resin's average degree of polymerization.

[0070] Similarly, Figures 3 and 4 illustrate the theoretical loss of intrinsic viscosity as a function of reactive carrier concentration at several molecular weights. Figure 3 depicts the impact of the reactive carrier upon polyethylene terephthalate having an intrinsic viscosity of 0.63 dl/g. Similarly, Figure 4 depicts the impact of the reactive carrier upon polyethylene terephthalate having intrinsic viscosity of 0.45 dl/g.

[0071] As will be understood by those of ordinary skill in the art, macromolecules having a degree of polymerization of about 70 are considered high polymers. For polyethylene terephthalate, this roughly translates to a molecular weight of at least about 13,000 g/mol. At this molecular weight, polyethylene terephthalate polymers possess sufficient molecular weight, mechanical properties, melt strength, and crystallinity to facilitate polymer processing.

[0072] In contrast, the reactive carriers according to the present invention have molecular weights that are

less than about 10,000 g/mol. The molecular weight of the reactive carrier is typically less than 6000 g/mol, preferably less than 4000 g/mol, more preferably between about 300 and 2000 g/mol, and most preferably between about 400 and 1000 g/mol. As used herein, molecular weight refers to number-average molecular weight, rather than weight-average molecular weight.

[0073] In general, reactive carriers having carboxyl, hydroxyl, or amine functional groups are favored. Suitable reactive carriers include esters (including low polymers derived from caprolactone), amides (including low polymers derived from caprolactam), imides, amines, isocyanates, oxazolines, acids, and anhydrides that are capable of reacting with the condensation polymers in a way that diminishes molecular weight loss of the condensation polymers during subsequent heated processes, such as injection molding and extrusion operations.

[0074] Also preferred are polyols, especially polyester polyols and polyether polyols, having a molecular weight that is sufficiently high such that the polyol will not substantially reduce the average molecular weight of the condensation polymers, and a viscosity that facilitates pumping of the polyol. Polyethylene glycol is a preferred polyol. Other exemplary polyols include functional polyethers, such as polypropylene glycol that is prepared from propylene oxide, random and block copolymers of ethylene oxide and propylene oxide, and polytetramethylene glycol that is derived from the polymerization of tetrahydrofuran.

[0075] Alternatively, the reactive carrier may also include dimer or trimer acids and anhydrides. In another embodiment, the reactive carrier may possess, in addition to or in place of terminal functional groups, internal functional groups (*e.g.*, esters, amides, and anhydrides) that react with the condensation polymers. In yet another embodiment, the reactive carrier may include esters without terminal functional groups, amides without terminal functional groups, or anhydrides without terminal functional groups that are capable of reacting into the condensation polymers during solid state polymerization and that will not cause the condensation polymers to suffer loss of molecular weight during injection molding or extrusion processes. As noted and as will be appreciated by those having ordinary skill in the art, reactive carriers derived from heterocycles (*e.g.*, caprolactone and caprolactam) are within the scope of the present invention.

[0076] It should be recognized that additives are sometimes marketed with oligomers that constitute an acceptable reactive carrier. For example, TINUVIN® 213, which is available from Ciba Specialty Chemicals, includes a hydroxyphenyl benzotriazole ultraviolet light absorber in a solution of unreacted polyethylene glycol having a molecular weight of 300 g/mol. As discussed previously, polyethylene glycol is a preferred reactive carrier. Accordingly, the present invention embraces the use of such premixed, additive/reactive carrier products.

[0077] An exemplary method according to the present invention includes reacting terephthalic acid and ethylene glycol in a heated esterification reaction to

form monomers and oligomers of terephthalic acid and ethylene glycol, then polymerizing these monomers and oligomers via melt phase polycondensation to form polyethylene terephthalate polymers. The polyethylene terephthalate polymers are then formed into chips (or pellets via a polymer cutter) and solid state polymerized. Thereafter, an additive is introduced at an extruder into the polyethylene terephthalate polymers using a reactive carrier, which facilitates uniform blending within the polymer melt. Preferably, the reactive carrier is a polyol (*e.g.*, polyethylene glycol) having a molecular weight that permits the polyol to be pumped at near ambient temperatures (*i.e.*, less than 60°C) and that is introduced to the polyethylene terephthalate polymers in quantities such that bulk properties of the polyethylene terephthalate polymers are not significantly affected. Importantly, the polyol reactive carrier combines with the polyethylene terephthalate polymer such that it is non-extractable during subsequent processing operations (*e.g.*, forming polyester beverage containers).

[0078] As noted, the invention embraces the late addition of various kinds of additives via the reactive carrier. Late addition is especially desirable where the additives are volatile or subject to thermal degradation. Conventional additive injection prior to polycondensation, such as during an esterification stage in the synthesis of polyester, or early during the polycondensation stage subjects additives to several hours of high-temperature (greater than 260°C) and reduced-pressure (less than 10 torr) conditions. Consequently, additives that have significant vapor

pressure at these conditions will be lost from the process. Advantageously, the method of the present invention significantly reduces the time additives are exposed to high polycondensation temperatures.

[0079] Additives according to the present invention can include preform heat-up rate enhancers, friction-reducing additives, stabilizers, inert particulate additives (*e.g.*, clays or silicas), colorants, antioxidants, branching agents, oxygen barrier agents, carbon dioxide barrier agents, oxygen scavengers, flame retardants, crystallization control agents, acetaldehyde reducing agents, impact modifiers, catalyst deactivators, melt strength enhancers, anti-static agents, lubricants, chain extenders, nucleating agents, solvents, fillers, and plasticizers.

[0080] In a preferred embodiment, the additive is an ultraviolet (UV) radiation absorber. As is understood by those familiar with polyester packaging, UV absorbers protect the polyethylene terephthalate polymers and contents of packages from UV degradation.

[0081] In another preferred embodiment, the additive is an inert particulate additive, preferably either talc (*i.e.*, a natural hydrous magnesium silicate of representative formula $3MgO{\bullet}4SiO_2{\bullet}H_2O$) or precipitated calcium carbonate. The inert particulate additive is introduced in low concentrations (*i.e.*, about 20 and 200 ppm based on the combined weight of the condensation polymers, the reactive carrier, and the inert particulate additive) to ensure that bottles formed from the condensation polymers possess reduced frictional

characteristics. Moreover, the inert particulate additive, which is preferably surface-treated to minimize haze formation in bottles, preferably has an average particle size of less than about ten microns, more preferably less than two microns. As described in commonly-assigned, copending U.S. Ser. No. 09/738,619, bottles formed from such polyethylene terephthalate condensation polymers have improved frictional characteristics that reduce, and can eliminate, the need to apply, during filling operations, external lubricants to polyester bottles.

[0082] In another preferred embodiment, the additive is an exfoliated clay nanocomposite, which enhances gas barrier properties in films and containers. Nanocomposites preferably are in the form of platelets having a thickness of between about 6 and 15 angstroms.

[0083] As will be known by those having skill in the art, polymerization catalysts increase polymerization rates, and thus productivity. Unfortunately, these same catalysts will eventually degrade the thermal stability of the polymer resin. Thus, in yet another embodiment, the additive carried by the reactive carrier is a catalyst stabilizer—more typically, extra catalyst stabilizer. In this regard, while phosphorous-containing stabilizers are preferred, any stabilizer that will deactivate the polymerization catalyst may be introduced via a reactive carrier. In general, the stabilizer should be non-reactive with the polymer and possess low residual moisture.

[0084] U. S. parent application Ser. No. 09/738,150 explains that as the polycondensation reaction of polyethylene terephthalate nears completion, the catalyst begins to form acetaldehyde and cause discoloration or yellowing of the polyethylene terephthalate. Accordingly, as discussed herein, thermally stable polyester refers to polyester having low acetaldehyde content, low discoloration, and high retention of molecular weight despite exposure to high temperatures.

[0085] Acetaldehyde is an objectionable byproduct of polyethylene terephthalate degradation. This is of particular concern to the food and beverage industry because acetaldehyde, even in minute amounts, adversely affects product taste. Moreover, polymer degradation will typically cause undesirable discoloration or yellowing. This is why a stabilizer, preferably containing phosphorous, is added to the polymer melt.

[0086] Advantageously, the late addition of the stabilizer to the polymer melt and then again at an extruder prevents the stabilizer from inhibiting ("cooling") the polymerization catalyst during the polycondensation reaction. This increases the production efficiency of continuous polyethylene terephthalate processes. Furthermore, because the stabilizer is added before polymer processing, the stabilizer can adequately prevent discoloration and degradation of the polyethylene terephthalate polyester.

[0087] Finally, it should be noted that because the melting and extruding steps in the formation of the condensation polymers are performed at elevated

temperatures (*e.g.*, usually greater than 260°C for polyethylene terephthalate), it is important that the condensation polymers be thermally stable. Accordingly, the stabilizer additive must be adequately blended with the polymer melt to deactivate polymerization catalysts. The reactive carrier facilitates the incorporation of the stabilizer into the polymer resin.

[0088] In the specification and the drawings, typical embodiments of the invention have been disclosed. Specific terms have been used only in a generic and descriptive sense, and not for purposes of limitation. The scope of the invention is set forth in the following claims.

CLAIMS:

1. A method for introducing additives into condensation polymers, comprising combining at an extruder condensation polymers having carbonyl functionality and a reactive carrier having a molecular weight of less than about 10,000 g/mol, the reactive carrier being the delivery vehicle for one or more additives.

2. A method according to Claim 1, further comprising polymerizing oligomeric precursors via melt phase polycondensation to form the condensation polymers having carbonyl functionality.

3. A method according to Claim 2, further comprising reacting a first polyfunctional component and a second polyfunctional component to form the oligomeric precursors to the condensation polymers, prior to the step of polymerizing the oligomeric precursors via melt phase polycondensation.

4. A method according to Claim 3, wherein the step of reacting a first polyfunctional component and a second polyfunctional component comprises reacting diacids and diols to form the oligomeric precursors.

5. A method according to Claim 3, wherein the step of reacting a first polyfunctional component and a second polyfunctional component comprises

reacting diesters and diols to form the oligomeric precursors.

6. A method according to Claim 3, wherein the step of reacting a first polyfunctional component and a second polyfunctional component comprises reacting diisocyanates and diols to form the oligomeric precursors.

7. A method according to Claim 3, wherein the step of reacting a first polyfunctional component and a second polyfunctional component comprises reacting diols and derivatives of carbonic acid to form the oligomeric precursors.

8. A method according to Claim 3, wherein the step of reacting a first polyfunctional component and a second polyfunctional component comprises reacting diacids and diamines to form the oligomeric precursors.

9. A method according to Claim 3, wherein the step of reacting a first polyfunctional component and a second polyfunctional component comprises reacting dianhydrides and diamines to form the oligomeric precursors.

10. A method according to Claim 3, wherein the step of reacting a first polyfunctional component and a second polyfunctional component comprises

reacting a terephthalate component and a diol component to form polyethylene terephthalate precursors.

11. A method according to Claim 10, wherein the step of reacting a terephthalate component and a diol component comprises:

reacting terephthalic acid and ethylene glycol in a heated esterification reaction to form monomers and oligomers of terephthalic acid and ethylene glycol, as well as water; and

removing water as it is formed during the esterification reaction to enable the esterification reaction to go essentially to completion.

12. A method according to Claim 10, wherein the step of reacting a terephthalate component and a diol component comprises:

reacting dimethyl terephthalate and ethylene glycol in a heated ester exchange reaction to form monomers and oligomers of terephthalate and ethylene glycol, as well as methanol; and

removing methanol as it is formed during the ester exchange reaction to enable the ester exchange reaction to go essentially to completion.

13. A method according to Claim 2, wherein the step of polymerizing the oligomeric precursors via melt phase polycondensation comprises self-polymerizing monomers possessing multi-functionality

to yield condensation polymers having carbonyl functionality.

14. A method according to Claim 1, wherein the reactive carrier is combined with the condensation polymers at the extruder in quantities such that bulk polymer properties of the condensation polymers are not significantly affected.

15. A method according to Claim 1, wherein the reactive carrier comprises a polyol.

16. A method according to Claim 15, wherein the polyol comprises polyethylene glycol.

17. A method according to Claim 1, wherein the reactive carrier is selected from the group consisting of esters, amides, imides, amines, isocyanates, oxazolines, acids, and anhydrides.

18. A method according to Claim 1, further comprising forming the condensation polymers and the reactive carrier into chips or pellets.

19. A method according to any of Claims 1-18, further comprising pelletizing the condensation polymers prior to the step of combining the condensation polymers and the reactive carrier.

20. A method according to Claim 19, further comprising solid state polymerizing the condensation polymers prior to the step of combining the condensation polymers and the reactive carrier.

21. A method according to any of Claims 1-17, further comprising pelletizing the condensation polymers and the reactive carrier.

22. A method according to any of Claims 1-18, further comprising solid state polymerizing the condensation polymers and the reactive carrier.

23. A method according to any of Claims 1-18, further comprising forming the condensation polymers and the reactive carrier into containers.

24. A method according to any of Claims 1-18, further comprising spinning the condensation polymers and the reactive carrier into fibers.

25. A method according to any of Claims 1-18, further comprising forming the condensation polymers and the reactive carrier into films.

26. A method according to any of Claims 1-5 or Claims 10-18, wherein the condensation polymers comprise a polyester.

27. A method according to Claim 26, wherein the polyester comprises polyethylene terephthalate.

28. A method according to any of Claims 1-3, Claim 6, or Claims 13-18, wherein the condensation polymers comprise a polyurethane.

29. A method according to any of Claims 1-3, Claim 7, or Claims 13-18, wherein the condensation polymers comprise a polycarbonate.

30. A method according to any of Claims 1-3, Claim 8, or Claims 13-18, wherein the condensation polymers comprise a polyamide.

31. A method according to any of Claims 1-3, Claim 9, or Claims 13-18, wherein the condensation polymers comprise a polyimide.

32. A method according to any of Claims 1-18, wherein the condensation polymers are a solid when combined with the reactive carrier at the extruder.

33. A method according to any of Claims 1-18, wherein the reactive carrier is a liquid or slurry when combined with the condensation polymers at the extruder.

34. A method according to Claim 33, wherein the reactive carrier is at near ambient temperature when combined with the condensation polymers.

35. A method according to any of Claims 1-18, wherein the reactive carrier is a solid when combined with the condensation polymers at the extruder.

36. A method according to any of Claims 1-18, wherein the step of combining at an extruder condensation polymers and a reactive carrier comprises introducing into the extruder the condensation polymers and the reactive carrier.

37. A method according to any of Claims 1-18, wherein the step of combining at an extruder condensation polymers and a reactive carrier comprises introducing the reactive carrier into the condensation polymers before the extruder, and then mixing the condensation polymers and the reactive carrier within the extruder.

38. A method according to any of Claims 1-18, wherein the step of combining at an extruder condensation polymers and a reactive carrier comprises introducing the reactive carrier into the condensation polymers after the extruder.

39. A method according to any of Claims 1-18, wherein the reactive carrier is combined with the condensation polymers at the extruder in quantities such that its concentration in the condensation polymers is less than about 10,000 ppm.

40. A method according to any of Claims 1-18, wherein the reactive carrier is combined with the condensation polymers at the extruder in quantities such that its concentration in the condensation polymers is less than about 1000 ppm.

41. A method according to any of Claims 1-18, wherein the reactive carrier is combined with the condensation polymers at the extruder in quantities such that its concentration in the condensation polymers is less than 500 ppm.

42. A method according to any of Claims 1-18, wherein the reactive carrier has a molecular weight of less than about 6000 g/mol.

43. A method according to any of Claims 1-18, wherein the reactive carrier has a molecular weight of less than about 4000 g/mol.

44. A method according to any of Claims 1-18, wherein the reactive carrier has a molecular weight of between about 300 and 2000 g/mol.

45. A method according to any of Claims 1-18, wherein the reactive carrier has a molecular weight of between about 400 and 1000 g/mol.

46. A method according to any of Claims 1-14 or Claim 18, wherein the reactive carrier comprises a polyol.

47. A method according to any of Claims 1-14 or Claim 18, wherein the reactive carrier is selected from the group consisting of dimer acids, dimer anhydrides, trimer acids, and trimer anhydrides.

48. A method according to any of Claims 1-14 or Claim 18, wherein the reactive carrier is a derivative or either caprolactone or caprolactam.

49. A method according to any of Claims 1-18, wherein the one or more additives comprise a UV absorber.

50. A method according to any of Claims 1-18, wherein the one or more additives comprise an additive that increases preform heat-up rate.

51. A method according to any of Claims 1-18, wherein the one or more additives comprise a phosphorous-containing stabilizer.

52. A method according to any of Claims 1-18, wherein the one or more additives comprise an oxygen scavenger.

53. A method according to any of Claims 1-18, wherein the one or more additives comprise an exfoliated clay nanocomposite.

54. A method according to any of Claims 1-18, wherein the one or more additives comprise between about 20 and 200 ppm of an inert particulate additive selected from the group consisting of talc and calcium carbonate, the inert particulate additive having an average particle size of less than about ten microns.

55. A method according to Claim 54, wherein the inert particulate additive is surface-modified.

56. A method according to any of Claims 1-18, wherein the one or more additives include an additive selected from the group consisting of friction-reducing additives, stabilizers, inert particulate additives, colorants, antioxidants, branching agents, barrier agents, flame retardants, crystallization control agents, acetaldehyde reducing agents, impact modifiers, catalyst deactivators, melt strength enhancers, anti-static agents, lubricants, chain extenders, nucleating agents, solvents, fillers, and plasticizers.

FIG. 1 (Impact of Reactive Carrier Molecular Weight on Condensation Polymers)

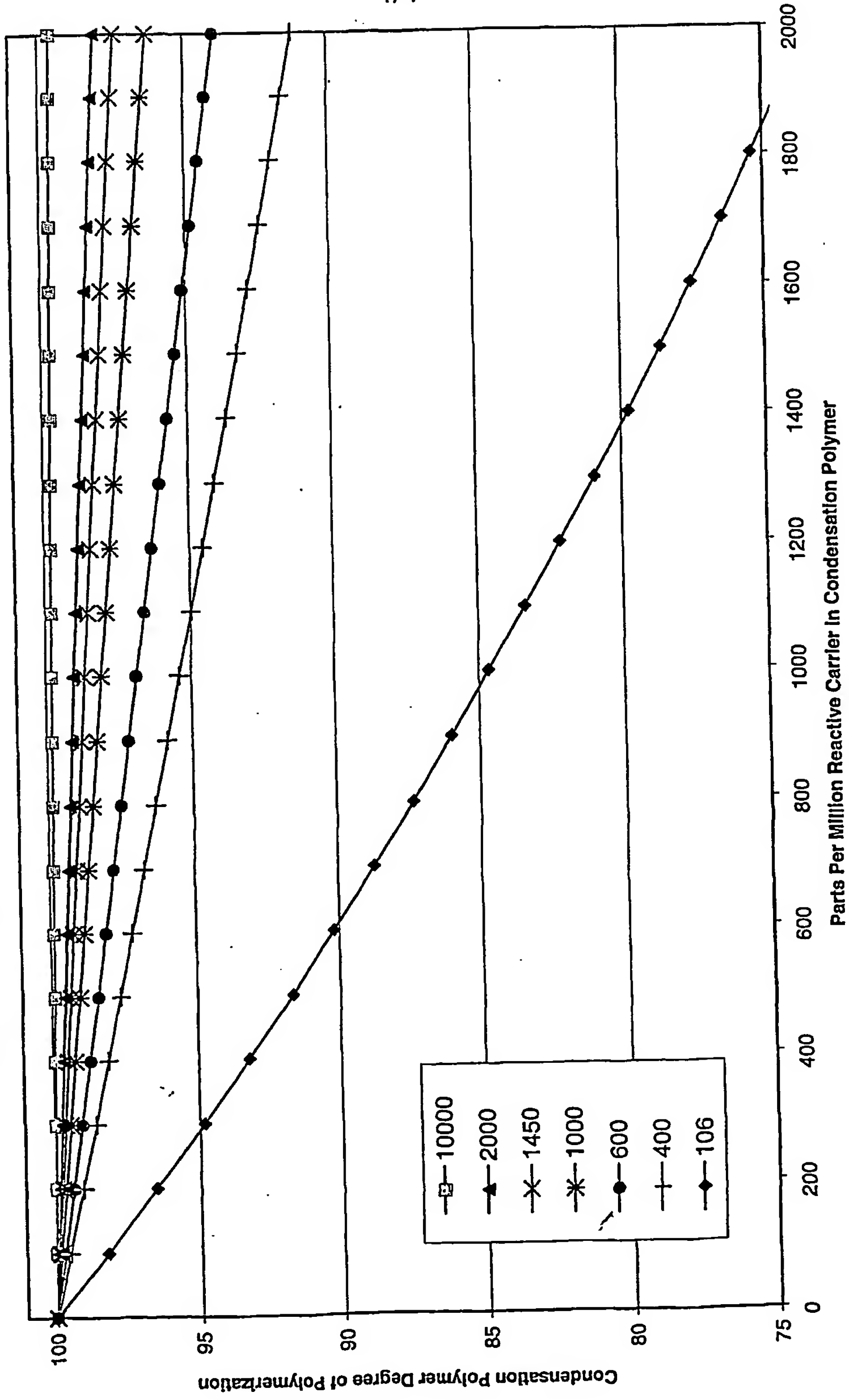


FIG. 2 (Impact of Reactive Carrier Molecular Weight on Condensation Polymers)

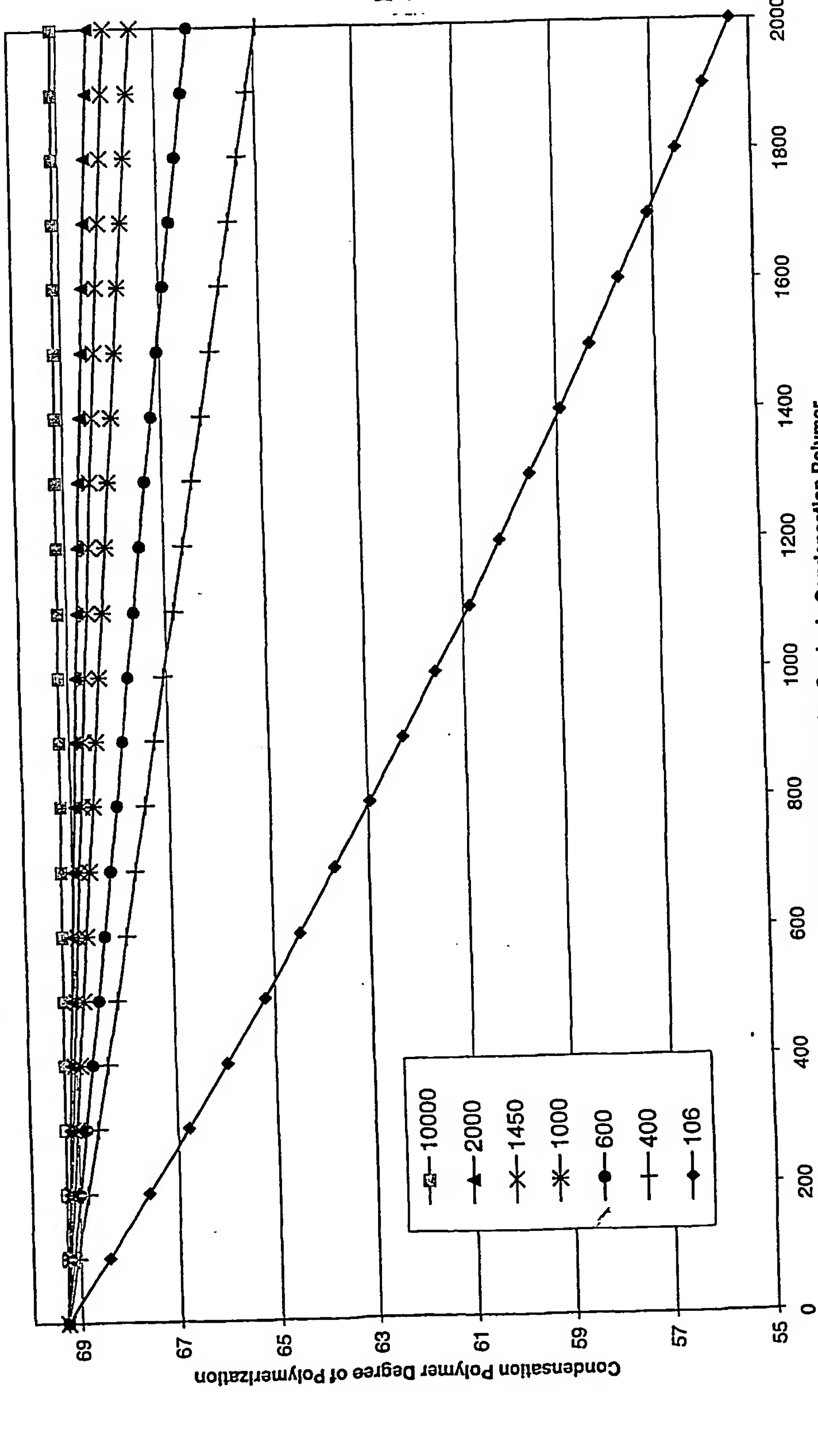


FIG. 3 (Impact of Reactive Carrier Molecular Weight upon Intrinsic Viscosity)

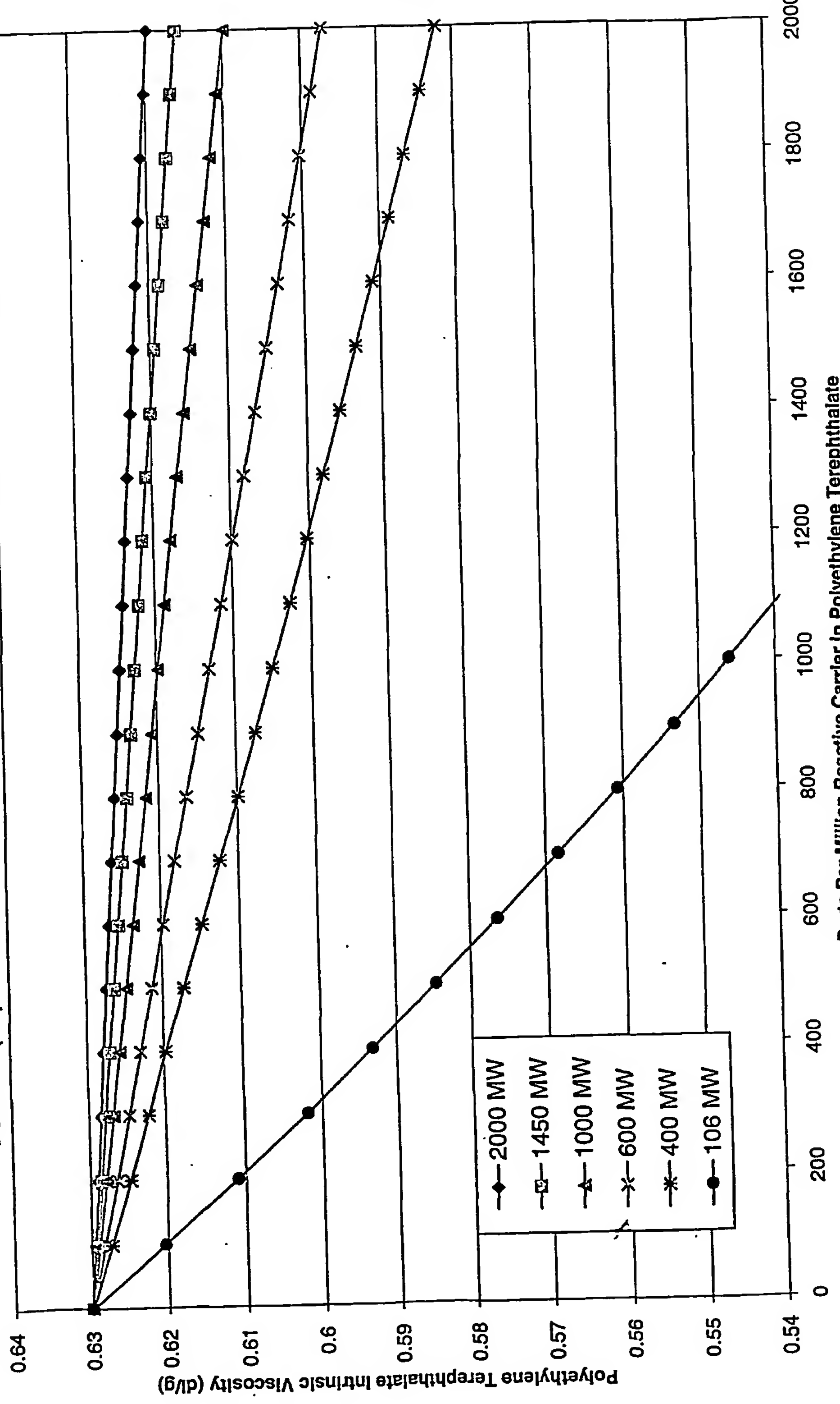


FIG. 4 (Impact of Reactive Carrier Molecular Weight upon Intrinsic Viscosity)